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Huig Klinkenberg, et. al

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For: PHOTOACTIVATABLE COATING
COMPOSITION AND ITS USE FOR THE
PREPARATION OF COATINGS WITH A
RAPIDLY PROCESSABLE SURFACE AT
AMBIENT TEMPERATURE

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Sir:

Enclosed herewith is a certified copy of European Patent Application No.
00201968.5, to support the claim of foreign priority benefits under 35 U.S.C.
§119 in connection with the above-identified application.

Respectfully submitted,

Joan M. McGillicuddy
Joan M. McGillicuddy
Attorney for Applicants
Reg. No.: 35,608

Akzo Nobel Inc.
Intellectual Property Department
7 Livingstone Avenue
Dobbs Ferry, New York 10522-3408
(914) 674-5463

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00201968.5

Der Präsident des Europäischen Patentamts;
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6824 BM Arnhem
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Photoactivatable coating composition and its use for the preparation of coatings with a rapidly processable surface at ambient temperature

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Photoactivatable coating composition and its use for the preparation of coatings with a rapidly processable surface at ambient temperature

- 5 The invention relates to a photoactivatable coating composition comprising (A) an activated unsaturated group-containing compound, (B) an activated CH group-containing compound, (C) a catalyst in the form of one or more Lewis or Brönstedt bases, with the conjugated acids of the latter having a pKa of at least 10, and (D) a photoinitiator, and to its use for the preparation of coatings with a
- 10 rapidly processable surface at ambient temperature.

A photoactivatable coating composition of the type indicated above is known from, int. al., EP-A-0 582 188. The coating layers produced with the coating compositions disclosed therein can be cured first by UV radiation and then, thoroughly, in a conventional manner at ambient temperature and/or by heating.

- 15 A key drawback of the known coating compositions is the simultaneous presence of at least two entirely different curing mechanisms. One mechanism is based on the reaction between CH-acid compounds and olefinically unsaturated compounds, which is preferably carried out in the presence of a base, whereas the other mechanism requires UV-radiation for curing a
- 20 radiation-curable oligomer with at least two (meth)acrylate groups. The latter mechanism can present serious problems in places which are not readily accessible to UV-light, such as three-dimensional surfaces, or where the presence of pigments does not allow the UV-radiation to penetrate into lower layers.

- 25 The invention now provides coating compositions which can be cured by UV-radiation without any problems occurring when the UV-light cannot reach all parts of the curable coating layer.

- 30 The photoactivatable coating composition according to the invention is characterised in that the photoinitiator is a photolabile base.

For radiation curing optimum results have been obtained thus far with the photolabile base being an α -amino alkene. Preference is given to a composition

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where the photolatent base (component (D)) is present in an amount from 0.01 to 10, and preferably 0.2 to 5, % by weight based on components (A) + (B).

Optimum results for the curing reaction of the unexposed parts have been obtained with a catalyst (C) in an amount of from 0.01 to 10, preferably 0.2 to 3,

5 % by weight based on components (A) + (B).

The coating compositions according to the invention are radiation curable after application and, optionally, evaporation of solvents. In particular, they are suitable for curing by irradiation with UV radiation. Combinations of IR/UV
10 irradiation are also suitable. Radiation sources which may be used are those customary for UV, such as high- and medium-pressure mercury lamps.

In order to avoid any risk involved in handling UV light of very short wave length (UV B and/or UV C light) preference is given, especially for use in automotive refinishing shops, to fluorescent lamps which produce the less injurious UV A
15 light. However, the intensity of the light produced by said lamps is too low to overcome oxygen inhibition of radically curing systems. Hence UV curing of coating compositions such as proposed in EP-A-0 582 188 does not perform efficiently.

Surprisingly, it has now been found that when a photolatent base is used as the
20 photoinitiator, more particularly when a sensitiser is also employed, there are no problems as a result of oxygen inhibition during irradiation with UV light from fluorescent lamps.

Suitable sensitisers are all compounds known to those skilled in the art as
25 sensitizers. Examples are e.g. thioxanthenes, such as isopropyl thioxanthone, 3-keto coumarines, oxazines, and rhodamines.

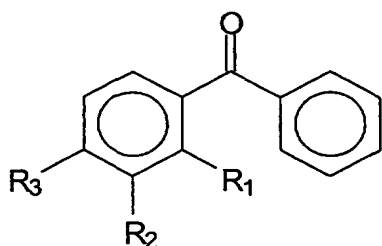
Surprisingly, it has been found that colourless surfaces can be obtained with benzophenone and derivatives thereof.

Examples of suitable derivatives of benzophenone are:

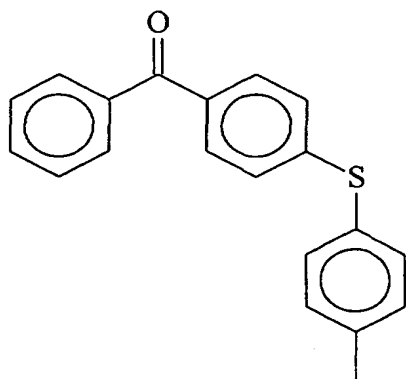
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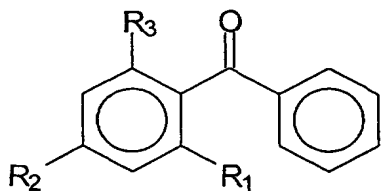
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wherein R_1 , R_2 , and R_3 may be the same or different and stand for CH_3 or H (e.g. Speedcure BEM[®] ex Lambson),



(e.g. Quantacure BMS[®] ex G. Lakes), and



5

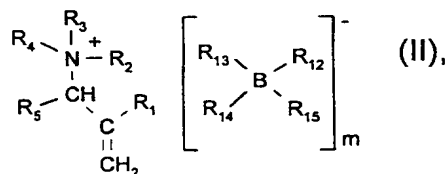
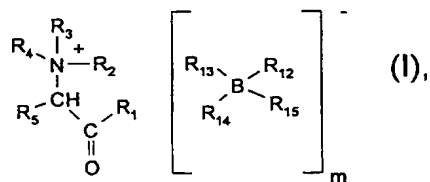
wherein R_1 , R_2 , and R_3 may be the same or different and stand for CH_3 or H (e.g. Esacure TZT[®] ex Lamberti).

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Examples of suitable photolabile bases (D) are

1) α -ammonium, α -iminium or α -amidinium salts of formula (I) or (II)



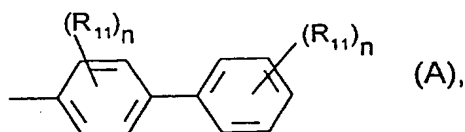
5

wherein

m is 1 or 2 and corresponds to the number of positive charges of the cation;

R₁ is phenyl, naphthyl, phenanthryl, anthracyl, pyrenyl, thienyl, thianthrenyl, thioxanthyl, fluorenyl or phenoxazinyl, these radicals being unsubstituted or

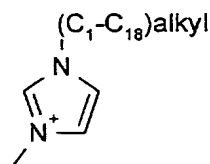
10 mono- or polysubstituted by C₁-C₁₈alkyl, C₃-C₁₈alkenyl, NR₆R₇, OH, CN, OR₈, SR₈, C(O)R₉, C(O)OR₁₀ or halogen, or **R₁** is a radical of formula A



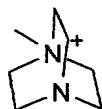
R₂, **R₃** and **R₄** are each independently of one another hydrogen, C₁-C₁₈alkyl, C₃-

C₁₈alkenyl or phenyl, or **R₂** and **R₃** and/or **R₄** and **R₃** form each independently of

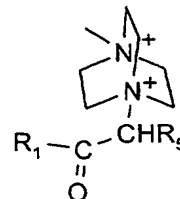
15 one another a C₂-C₁₂alkylene bridge; or **R₂**, **R₃**, **R₄**, together with the linking nitrogen atom, are a group of the structural formula (a), (b), (c), or (d)



(a),



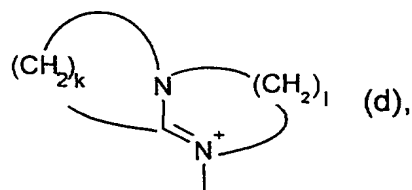
(b),



(c),

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k and l are each independently of the other a number from 2 to 4;

R₅, R₆, R₇, R₈, R₉ and R₁₀ are hydrogen or C₁-C₁₈alkyl;

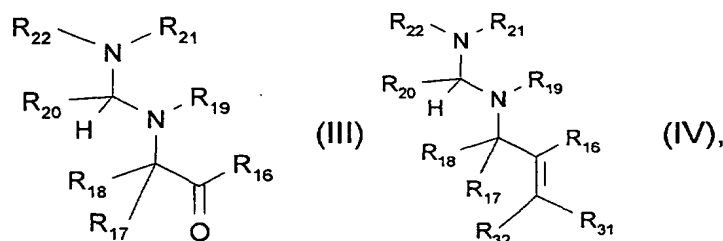
R₁₁ is C₁-C₁₈alkyl, C₂-C₁₈alkenyl, NR₆R₇, OR₈, or SR₈; and

5 n is 0 or 1, 2 or 3;

R₁₂, R₁₃ and R₁₄ is phenyl or another aromatic hydrocarbon, these radicals being unsubstituted or mono- or polysubstituted by C₁-C₁₈alkyl, OR₈, or halogen;

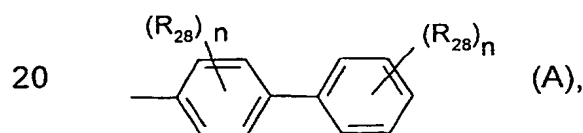
10 R₁₅ is C₁-C₁₈alkyl, phenyl or another aromatic hydrocarbon, the radicals phenyl and aromatic hydrocarbon being unsubstituted or mono- or polysubstituted by C₁-C₁₈alkyl, OR₈, or halogen.

2) Compounds of formula (III) or (IV)



15 in which

R₁₆ is phenyl, naphthyl, phenanthryl, anthracyl, pyrenyl, thienyl, thianthrenyl, thioxanthyl, fluorenyl or phenoxazinyl, these radicals being unsubstituted or mono- or polysubstituted by C₁-C₁₈alkyl, C₃-C₁₈alkenyl, NR₂₃R₂₄, OH, CN, OR₂₅, SR₂₅, C(O)R₂₆, C(O)OR₂₇ or halogen, or R₁₆ is a radical of formula A



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R_{17} and R_{18} independently of one another are hydrogen, C_1 - C_{18} alkyl, C_3 - C_{18} alkenyl, C_3 - C_{18} alkynyl or phenyl;

R_{20} is C_1 - C_{18} alkyl or $NR_{29}R_{30}$;

R_{19} , R_{21} , R_{22} , R_{29} and R_{30} independently of one another are hydrogen or C_1 -

5 C_{18} alkyl; or

R_{19} and R_{21} together form a C_2 - C_{12} alkylene bridge or

R_{20} and R_{22} together, independently of R_{19} and R_{21} , form a C_2 - C_{12} alkylene bridge or, if R_{20} is $NR_{29}R_{30}$, R_{30} and R_{22} together form a C_2 - C_{12} alkylene bridge.

R_{31} is hydrogen or C_1 - C_{18} alkyl;

10 R_{32} is hydrogen, C_1 - C_{18} alkyl or phenyl substituted by C_1 - C_{18} alkyl.

Preferred compounds are

1) α -ammonium, α -iminium or α -amidinium salts of formula (I) or (II)

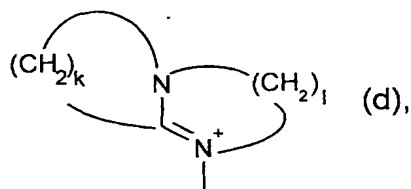
wherein

m is 1

15 R_1 is phenyl, or naphthyl, these radicals being unsubstituted or mono- or polysubstituted by C_1 - C_6 alkyl, OR_8 , SR_8 ,

R_2 , R_3 and R_4 are each independently of one another hydrogen, C_1 - C_{18} alkyl, or phenyl, or R_2 and R_3 and/or R_4 and R_3 form each independently of one another a C_2 - C_6 alkylene bridge; or R_2 , R_3 , R_4 , together with the linking nitrogen atom,

20 are a group of the structural formula (d),



k and l are each independently of the other a number from 2 to 4;

R_5 and R_8 are hydrogen or C_1 - C_6 alkyl;

25 R_{12} , R_{13} , R_{14} and R_{15} is phenyl or another aromatic hydrocarbon, these radicals being unsubstituted or mono- or polysubstituted by C_1 - C_6 alkyl or halogen.

2) compounds of formula (III) or (IV)

wherein

R_{16} is phenyl, or naphthyl, these radicals being unsubstituted or mono- or polysubstituted by C_1 - C_6 alkyl, OR_{25} , SR_{25} ,

5 R_{17} and R_{18} are hydrogen or C_1 - C_6 alkyl;

R_{19} and R_{21} together form a C_2 - C_6 alkylene bridge;

R_{20} and R_{22} together form a C_2 - C_6 alkylene bridge;

R_{25} is hydrogen or C_1 - C_6 alkyl

R_{31} and R_{32} are hydrogen.

10 Thus far optimum results have been obtained when the compounds of formula (IV) are used, wherein

R_{16} is phenyl ;

R_{17} and R_{18} are hydrogen or methyl;

R_{19} and R_{21} together form a C_3 -alkylene bridge;

15 R_{20} and R_{22} together form a C_3 -alkylene bridge;

R_{31} and R_{32} are hydrogen.

For compound (C) optimum results have been found thus far with both electrically neutral and electrically charged bases.

Suitable catalysts include electrically neutral bases such as amines and derivatives thereof. It is preferred that use be made of a base of which the conjugated acid has a pK_a of at least 12, such as amines of the amidine type, examples of which include tetramethyl guanidine, 1,4-dihydropyrimidines, 1,8-diazabicyclo-[5,4,0]-undec-7-ene, 1,5-diazabicyclo-[4.3.0]-non-5-ene (DBN), and 2-alkyl-N-alkylimidazoline. Thus far, optimum results have been obtained
20 with diazabicycloundecene (DBU).

According to the invention, electrically charged bases also constitute suitable catalysts, provided that the conjugated acid thereof has a $pK_a > 10$, preferably > 12 . As examples of representative bases may be mentioned metal bases and quaternary ammonium bases. Examples of suitable bases include metal

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- alcoholates such as sodium methanolate or sodium phenolate; metal hydroxides such as sodium hydroxide; metal hydrocarbon compounds such as n-butyl lithium; metal hydrides such as sodium hydride; metal amides such as potassium amide; metal carbonates such as potassium carbonate; quaternary ammonium hydroxides such as tetrabutyl ammonium hydroxide; quaternary ammonium alkoxides such as benzyltrimethyl ammonium methoxide, and quaternary ammonium carbanions such as benzyltrimethyl ammonium acetyl acetate.
- 5
- 10 Suitable activated unsaturated group-containing compounds generally are ethylenically unsaturated compounds in which the carbon-carbon double bond is activated by a carbonyl group in the α -position. As representative examples may be mentioned such compounds disclosed in US-A-2759913 (see especially col. 6, line 35 through col. 7, line 45), US-A-4871822 (see especially col. 2, line 14 through col. 4, line 14), US-A-4602061 (see especially col. 3, line 14 through col. 4, line 14), and EP-A-0448154 (see especially page 2, line 53 through page 3, line 28).
- 15
- Suitable examples are the (meth)acrylic esters of compounds containing 1-6 hydroxyl groups and 1-20 carbon atoms. Instead of or in addition to (meth)acrylic acid there may be used, for example, crotonic acid and cinnamic acid. These esters may optionally contain hydroxyl groups. Especially preferred examples include hexanediol diacrylate, trimethylolpropane triacrylate, and pentaerythritol tetraacrylate.
- 20
- 25 Other examples are polyesters based upon maleic, fumaric and/or itaconic acid (and maleic and itaconic anhydride), and di- or polyvalent hydroxyl compounds, optionally including a monovalent hydroxyl and/or carboxyl compound.
- 30 Further suitable activated unsaturated group-containing compounds are polyester and/or alkyd resins containing pendant activated unsaturated groups.

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Preference is given to urethane (meth)acrylates obtained by reaction of a polyisocyanate with a hydroxyl group-containing (meth)acrylic ester, e.g., a hydroxyalkyl ester of (meth)acrylic acid or a compound prepared by esterification of a polyhydroxyl compound with a less than stoichiometric amount of (meth)acrylic acid; polyether (meth)acrylates obtained by esterification of a hydroxyl group-containing polyether with (meth)acrylic acid; polyfunctional (meth)acrylates obtained by reaction of a hydroxyalkyl (meth)acrylate with a polycarboxylic acid and/or a polyamino resin; poly(meth)acrylates obtained by reaction of (meth)acrylic acid with an epoxy resin, and polyalkylmaleates obtained by reaction of a monoalkylmaleate ester with an epoxy resin and/or a hydroxy-functional oligomer or polymer.

Especially preferred among the activated unsaturated group-containing compounds are the aforementioned poly(meth)acrylates obtained by the reaction of (meth)acrylic acid with an epoxy resin.

Also, preference is given to coating compositions where the acid value of the activated unsaturated group-containing compounds is about 2 or less.

Suitable activated CH group-containing compounds generally are compounds containing a methylene and/or monosubstituted methylene group in the α -position to two carbonyl groups, such as malonate and/or acetoacetate group-containing compounds.

Examples of malonate group-containing compounds are disclosed in US-A-2,759,913 (see especially col. 8, lines 51-52), and malonate group-containing oligomeric and polymeric compounds as disclosed in US-A-4,602,061 (see especially col. 1, line 10 through col. 2, line 13). Preferred compounds are the oligomeric and/or polymeric malonate group-containing compounds such as polyurethanes, polyesters, polyacrylates, epoxy resins, polyamides, and polyvinyl resins which contain malonate groups in the main chain or are pendant or both.

30

Malonate group-containing polyurethanes can be obtained, for example, by reacting a polyisocyanate with a hydroxyl group-containing ester of a polyol and malonic acid, or by esterification or transesterification of a hydroxy-functional polyurethane with malonic acid or a dialkylmalonate.

5

Malonate group-containing polyesters can be obtained, for example, by the polycondensation of malonic acid, an alkyl malonic acid (such as ethyl malonic acid), a mono- or dialkyl ester of such a malonic acid and/or the reaction product of a malonic ester and an alkyl (meth)acrylate, optionally with other di- or polycarboxylic acids, with di- and/or higher-functional hydroxy compounds, and, optionally, monofunctional hydroxy and/or carboxyl compounds.

10

Malonate group-containing epoxy esters can be obtained, for example, by esterifying an epoxy resin with malonic acid or a malonic monoester, or by transesterification with a dialkyl malonate, optionally with other carboxylic acids and derivatives thereof.

15

Malonate group-containing polyamides can be obtained, for example, in the same manner as the polyesters, in which case at least part of the hydroxy compound is replaced with a mono- and/or polyvalent primary and/or secondary amine.

20

Other malonate group-containing polymers can be obtained by the transesterification of an excess of a dialkyl malonate with a hydroxy-functional polymer, for example, a vinyl alcohol/styrene copolymer. In this manner, a polymer with malonate group-containing side-chains may be formed. Any excess dialkyl malonate can be removed under reduced pressure or, optionally, may be used as a reactive solvent.

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Use can also be made of these malonate group-containing compounds in which the malonic acid structural unit is cyclised, for example by formaldehyde, acetaldehyde, acetone or cyclohexanone.

- 5 Preference is given to malonate group-containing oligomeric esters, polyesters, polyurethanes, and epoxy esters containing 2-100, more preferably 2-20, malonate groups per molecule. In said case preference is given to compounds having a number average molecular weight (M_n) in the range of from about 250 to about 3,000, and an acid number of about 2 or less.

10

- As examples of acetoacetate group-containing compounds may be mentioned acetoacetic esters as disclosed in US-A-2,759,913 (see especially col. 8, lines 53-54), diacetoacetate compounds as disclosed in US-A-4,217,396 (see especially col.2, line 65 through col. 3, line 27), and acetoacetate group-
15 containing oligomeric and polymeric compounds as disclosed in US-A-4,408,018 (see especially col.1, line 51 through col. 2, line 6). Preference is given to the oligomeric and/or polymeric acetoacetate group-containing compounds.

- 20 Suitable acetoacetate group-containing oligomeric and polymeric compounds can be obtained, for example, from polyalcohols and/or hydroxy-functional polyether, polyester, polyacrylate, vinyl and epoxy oligomers and polymers by reaction with diketene or transesterification with an alkyl acetoacetate. Such compounds can also be obtained by the copolymerisation of an acetoacetate-
25 functional acrylic monomer with other vinyl- and/or acrylic-functional monomers.

- Especially preferred among the acetoacetate group-containing compounds for use with the present invention are acetoacetate group-containing oligomers and polymers containing at least 2 acetoacetate groups. It is also especially
30 preferred that such acetoacetate group-containing compounds have an M_n in

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the range of from about 234 to about 30,000, and an acid number of about 2 or less.

Compounds containing both malonate and acetoacetate groups in the same molecule are also suitable and can be obtained, for example, by a Michael reaction between a malonate-functional polyester and an acetoacetate-functional acrylic compound (e.g., acetoacetoxyethyl acrylate). Additionally, physical mixtures of malonate and acetoacetate group-containing compounds are suitable. Alkylacetoacetates can, in addition, be used as reactive diluents.

10

Optionally, the activated CH groups-containing compounds may be utilised in the enamine form, such as disclosed in EP-A-0 420 133.

As stated hereinbefore, components (A) and (B) react with each other through a Michael addition, in which the activated CH group of component (B) adds to one of the carbon atoms of the activated unsaturated group of component (A). Components (A) and (B) preferably are present in the coating compositions in an amount such that the ratio of the number of activated CH groups to the number of activated unsaturated groups is in the range of about 0.25 to about 4.0, more preferably in the range of about 0.5 to about 2.0.

The use of α -amino alkenes as photolabile base in coating compositions containing both activated unsaturated group-containing compounds and activated CH group-containing compounds has been disclosed in WO 98/41524 (see especially pages 1, 14, and 36-37). However, not the slightest allusion is made therein to the combined use of a photolabile base and an unblocked base.

The coating composition of the present invention may be applied to any substrate. The substrate may be, for example, metal, plastic, wood, glass, ceramic, or another coating layer. The other coating layer may be comprised of the coating composition of the current invention or it may be a different coating

composition. The coating compositions of the current invention show particular utility as clearcoats, basecoats, pigmented topcoats, primers, and fillers. The coating compositions can be applied by conventional means such as by spray gun, brush, or roller, spraying being preferred. Curing temperatures are preferably between 0 and 80°C, and more preferably between 20 and 60°C. The compositions are particularly suitable in the preparation of coated metal substrates, such as in the refinish industry, in particular the body shop, to repair automobiles and transportation vehicles and in finishing large transportation vehicles such as trains, trucks, buses, and aeroplanes.

10

Preferred is the use of the coating composition of the present invention as clearcoat. Clearcoats are required to be highly transparent and must adhere well to the basecoat layer. It is further required that the clearcoat does not change the aesthetic aspect of the basecoat by strike-in, i.e. discolouration of the basecoat due to its solvation by the clearcoat composition, or by yellowing of the clearcoat upon outdoor exposure. A clearcoat based on the coating composition of the present invention does not have these drawbacks.

15

In the case of the coating composition being a clearcoat, the basecoat may be a conventional basecoat known in the coating art. Examples are solvent borne basecoats, e.g., Autobase[®] ex Sikkens, based on cellulose acetobutyrate, acrylic resins, and melamine resins, and water borne basecoats, e.g., Autowave[®] ex Sikkens, based on an acrylic resin dispersion and polyester resin. Furthermore, the basecoat may comprise pigments (colour pigments, metallics and/or pearls), wax, solvents, flow additives, neutralizing agent, and defoamers. Also high-solid basecoats can be used. These are, for instance, based on polyols, imines, and isocyanates. The clearcoat composition is then applied to the surface of a basecoat and then cured. An intermediate curing step for the basecoat may be introduced.

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The invention will be illustrated with reference to the following examples. Of course these examples are submitted for a better understanding of the invention only; they are not to be construed as limiting in any manner the scope thereof.

5 EXAMPLES

(A) Preparation of a urethane acrylate based on the trimer of isophorone diisocyanate (IPDI trimer) and 4-hydroxybutyl acrylate.

The reaction was carried out under a dry air atmosphere and all commercial
10 chemicals used were employed without further purification.

3,637.0 g (10.5 moles of NCO) of the trimer of isophorone diisocyanate (Vestanat T 1890[®] ex Hüls), 2.6 g of dibutyltin dilaurate, 2.6 g of 2,5-di-tert.-butyl-p-cresol, and 300 g of butyl acetate were charged to a three-necked flask with condenser and dropping device. Dry air was bubbled through the reaction
15 mixture and the temperature was slowly raised to 60°C. 1,514.0 g (10.5 moles) of 4-hydroxybutyl acrylate were added, with the temperature gradually being increased to 80°C. The temperature was kept at said value and the dropping device was flushed with butyl acetate (500 g). The reaction was monitored by titration of the remaining amount of isocyanate and was over when the
20 isocyanate content fell below 0.2% based on the solids content. The reaction product obtained had the following physical properties:

Residual 4-hydroxybutyl acrylate: < 0.28% based on solids (HPLC analysis),

Colour: Gardner << Gardner 1,

Viscosity: 478 cPa s (23 °C),

25 Solids content: 72.8 % (1 hour at 140°C),

GPC data (polystyrene standard): Mn 1,507, Mw 1,814, d=1.2.

Equivalent weight = 527 g/eq

(B) Preparation of activated unsaturated group-containing compound.

30 The reaction was carried out under a nitrogen atmosphere and all commercial chemicals used were employed without further purification.

In a reaction vessel with stirrer and condenser 1,045 g of 1,5-pentanediol, 1,377.4 g of diethyl malonate, and 242.1 g of xylene were carefully refluxed. The maximum temperature of the reaction mixture was 196°C while the temperature at the head of the condenser was held at 79°C. In this way 862 g of ethanol, corresponding to a conversion of 97.7%, were distilled off. Then xylene was stripped off *in vacuo* at a temperature of 200°C. The resulting polymer had a solids content of 98.6%, a viscosity of 2,710 mPa s, and an acid number of 0.3 mg of KOH/g based on the solids content.

$M_n = 1,838$, $M_w = 3,186$, colour 175 on the APHA scale ("Hazen colour number" - ISO 6271 of the American Health Association).

Equivalent weight = 190 g/eq

Curing with UV light

The photoinitiator of claim 7 (= Example A5 of WO 98/41524), the sensitiser Quantacure BMS[®], and the uncapped base diazabicycloundecene (DBU) were dissolved in a mixture of the above-described urethane acrylate and the malonate polyester at an equivalent ratio of 1.3:1 such that the weight percentage of the latent base was 2.5% (based on solid resin) and that of Quantacure BMS[®] 0.5% (based on solid resin). The amount of DBU was constantly varied from 0 up to 5 wt.%.

A 50 µm thick film was drawn out onto a glass plate and exposed to UV-A light (fluorescent lamps, type Cleo[®] ex Philips) at a distance of 20 cm. The results of the experiments carried out at ambient temperature both in the dark and after 10 minutes' exposure are given in Table 1. The percentages quoted in the examples denote percentages by weight, and parts are parts by weight.

The times mentioned in the columns under "drying" correspond to the times until a tack-free surface had been obtained.

The times mentioned in the last column under "pot life" correspond to the times elapsed after the viscosity had doubled.

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Table 1

% DBU on solid resin	%latent base on solid resin	Quantacure on solid resin	drying after exposure	drying in the darkness	pot life
0	0	0	> 1 day	> 1 day	> 1 week
0	2.5	0.5	10 minutes	> 1 day	> 1 week
0.5	2.5	0.5	10 minutes	> 90 min.	6 hours
1	2.5	0.5	10 minutes	90 minutes	5 hours
2.5	2.5	0.5	10 minutes	55 minutes	2 hours
5	2.5	0.5	10 minutes	35 minutes	45 minutes

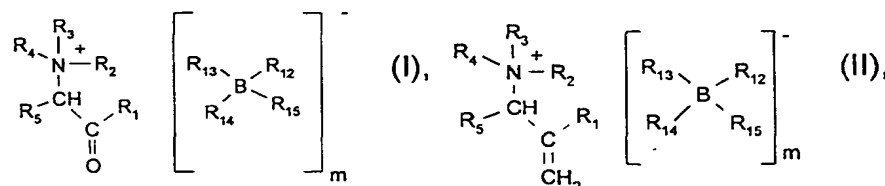
According to the results mentioned in the above table, it appears that the combined use of DBU and the latent base does not have a negative effect on drying after exposure. However, the drying in the darkness increases with increasing DBU concentration. Up to a percentage of about 2.5 DBU the pot life is still acceptable. A percentage of 5 wt.% is attended with a pot life of only 45 minutes. For commercial application such a short pot life may be questionable for a number of applications.

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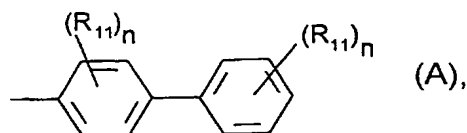
Claims

1. Photoactivatable coating composition comprising
 (A) an activated unsaturated group-containing compound, (B) an
 5 activated CH group-containing compound, (C) a catalyst in the form of
 one or more Lewis or Brönstedt bases, with the conjugated acids of the
 latter having a pKa of at least 10, and (D) a photoinitiator, characterised
 in that the photoinitiator is a photolabile base.
- 10 2. A coating composition according to claim 1, characterised in that the
 photolabile base is
- 1) an α -ammonium, α -iminium or α -amidinium salt of formula (I) or (II)



wherein

- 15 m is 1 or 2 and corresponds to the number of positive charges of the
 cation;
- R_1 is phenyl, naphthyl, phenanthryl, anthracyl, pyrenyl, thienyl,
 thianthrenyl, thioxanthyl, fluorenyl or phenoxazinyl, these radicals being
 unsubstituted or mono- or polysubstituted by C_1 - C_{18} alkyl, C_3 - C_{18} alkenyl,
 20 NR_6R_7 , OH, CN, OR_8 , SR_8 , $C(O)R_9$, $C(O)OR_{10}$ or halogen, or R_1 is a
 radical of formula A

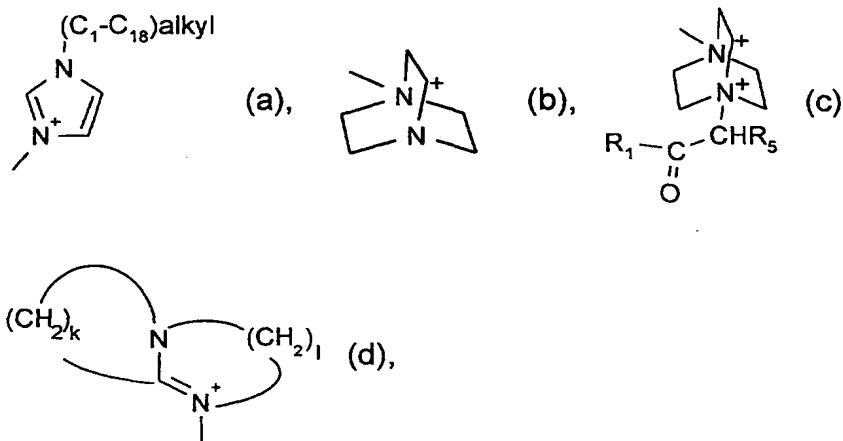


- 25 R_2 , R_3 and R_4 are each independently of one another hydrogen, C_1 -
 C_{18} alkyl, C_3 - C_{18} alkenyl or phenyl, or R_2 and R_3 and/or R_4 and R_3 form
 each independently of one another a C_2 - C_{12} alkylene bridge; or R_2 , R_3 ,

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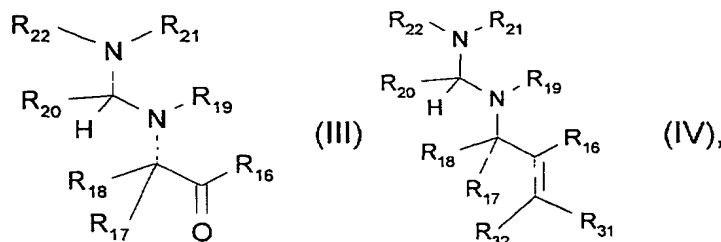
R_4 , together with the linking nitrogen atom, are a group of the structural formula (a), (b), (c), or (d)



- 5 k and l are each independently of the other a number from 2 to 4;
 R_5 , R_6 , R_7 , R_8 , R_9 and R_{10} are hydrogen or C_1-C_{18} alkyl;
 R_{11} is C_1-C_{18} alkyl, C_2-C_{18} alkenyl, NR_6R_7 , OR_8 , or SR_8 ; and
 n is 0 or 1, 2 or 3;
 R_{12} , R_{13} and R_{14} is phenyl or another aromatic hydrocarbon, these
10 radicals being unsubstituted or mono- or polysubstituted by C_1-C_{18} alkyl,
 OR_8 , or halogen;
 R_{15} is C_1-C_{18} alkyl, phenyl or another aromatic hydrocarbon, the radicals
phenyl and aromatic hydrocarbon being unsubstituted or mono- or
polysubstituted by C_1-C_{18} alkyl, OR_8 , or halogen;

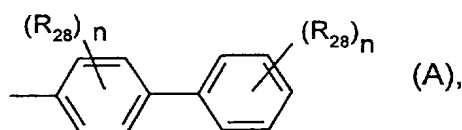
15 or

2) a compound of formula (III) or (IV)



in which

R_{16} is phenyl, naphthyl, phenanthryl, anthracyl, pyrenyl, thienyl, thianthrenyl, thioxanthyl, fluorenyl or phenoxazinyl, these radicals being unsubstituted or mono- or polysubstituted by C_1 - C_{18} alkyl, C_3 - C_{18} alkenyl, $NR_{23}R_{24}$, OH, CN, OR_{25} , SR_{25} , $C(O)R_{26}$, $C(O)OR_{27}$ or halogen, or R_{16} is a radical of formula A



R_{17} and R_{18} independently of one another are hydrogen, C_1 - C_{18} alkyl, C_3 - C_{18} alkenyl, C_3 - C_{18} alkynyl or phenyl;

R_{20} is C_1 - C_{18} alkyl or $NR_{29}R_{30}$;

R_{19} , R_{21} , R_{22} , R_{29} and R_{30} independently of one another are hydrogen or C_1 - C_{18} alkyl; or

R_{19} and R_{21} together form a C_2 - C_{12} alkylene bridge or

R_{20} and R_{22} together, independently of R_{19} and R_{21} , form a C_2 -

C_{12} alkylene bridge or, if R_{20} is $NR_{29}R_{30}$, R_{30} and R_{22} together form a C_2 - C_{12} alkylene bridge.

R_{31} is hydrogen or C_1 - C_{18} alkyl;

R_{32} is hydrogen, C_1 - C_{18} alkyl or phenyl

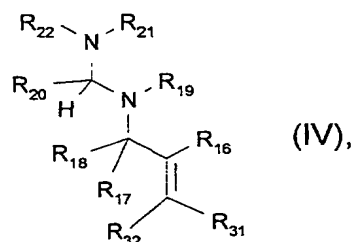
3. A coating composition according to claim 1, characterised in that component (D) is present in an amount of from 0.01 to 10% by weight based on components (A) + (B).

4. A coating composition according to claim 1, characterised in that component (C) is present in an amount of from 0.01 to 10% by weight based on components (A) + (B).

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5. A coating composition according to claim 1, characterised in that the composition additionally comprises a sensitiser selected from the group of thioxanthenes, oxazines, 3-ketocoumarins and rhodamines.
- 5 6. A coating composition according to claim 1, characterised in that the composition additionally comprises a sensitiser selected from the group of benzophenone and derivatives thereof.
7. A coating composition according to claim 1, characterised in that the
10 photolabile base is an α -aminoalkene of the structure (IV),



wherein

R_{16} is phenyl ;

R_{17} and R_{18} are hydrogen or methyl;

15 R_{19} and R_{21} together form a C_3 -alkylene bridge;

R_{20} and R_{22} together form a C_3 -alkylene bridge;

R_{31} and R_{32} are hydrogen.

8. A coating composition according to claim 7, characterised in that the
20 composition additionally comprises a sensitiser.
9. A coating composition according to claim 1, characterised in that (C) is diazabicycloundecene.
- 25 10. A coating composition according to claim 1, characterised in that the compound with an activated CH group is an oligomeric or polymeric

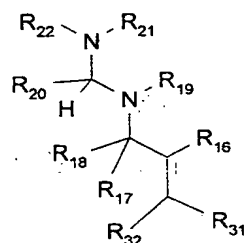
malonate compound and/or an acetoacetate group-containing compound.

- 5 11. A coating composition according to claim 10, characterised in that the malonate compound is a polyurethane, a polyester, a polyacrylate, an epoxy resin, a polyimide or a polyvinyl resin with malonate groups in the main and/or side chain.
- 10 12. A coating composition according to claim 10, characterised in that (A) and (B) are present in an amount such that the ratio of the number of activated CH groups to the number of activated unsaturated groups is in the range of about 0.25 to about 4.0.
- 15 13. A coating composition according to claim 12, characterised in that (A) and (B) are present in an amount such that the ratio of the number of activated CH groups to the number of activated unsaturated groups is in the range of about 0.5 to about 2.0.
- 20 14. A coating composition according to claim 1, characterised in that (C) and (D) are present in an amount such that their weight ratio is in the range of about 0.1 to about 2.5.

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Abstract

- Photoactivatable coating composition comprising (A) an activated unsaturated group-containing compound, (B) an activated CH group-containing compound
5 such as an oligomeric or polymeric malonate compound and/or an acetoacetate group-containing compound, (C) a catalyst in the form of one or more Lewis or Brönstedt bases, with the conjugated acids of the latter having a pKa of at least 10, such as diazabicycloundecene and (D) a photoinitiator, wherein the photoinitiator is a photolabile base. Preference is given to a coating composition
10 wherein the photolabile base is an α -aminoalkene of the structure



wherein R_{16} is phenyl; R_{17} and R_{18} are hydrogen or methyl; R_{19} and R_{21} together form a C_3 -alkylene bridge; R_{20} and R_{22} together form a C_3 -alkylene bridge; R_{31} and R_{32} are hydrogen.

- 15 The composition additionally comprises a sensitiser selected from the group of thioxanthenes, oxazines, rhodamines, 3-ketocoumarins and preferably from the group of benzophenone and derivatives thereof.

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